

AD-A154 317 ELECTROCHEMICAL STUDIES IN LIQUID CRYSTALS(U) CORNELL 1/1  
UNIV ITHACA NY DEPT OF CHEMISTRY R D MARIANI ET AL.  
10 APR 85 TR-1 N00014-84-K-0656

UNCLASSIFIED

F/G 7/4

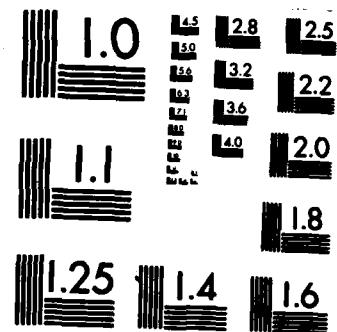
NL



END

END

END



MICROCOPY RESOLUTION TEST CHART  
NATIONAL BUREAU OF STANDARDS-1963-A

**AD-A154 317**

(2)

OFFICE OF NAVAL RESEARCH  
CONTRACT N00014-84-K-0656  
TASK NO. NR 627-844  
TECHNICAL REPORT #1

ELECTROCHEMICAL STUDIES IN LIQUID CRYSTALS

by

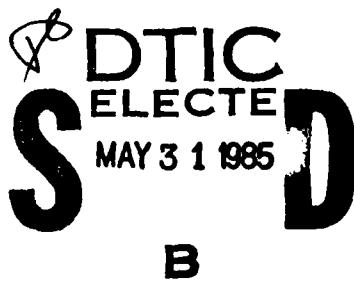
Robert D. Mariani, Angela Serra and Hector D. Abruna\*

Department of Chemistry  
Cornell University  
Ithaca, New York 14853

April 10, 1985

Reproduction in whole or in part is permitted for  
any purpose of the United States Government

This document has been approved for public release and sale;  
its distribution is unlimited



**DTIC FILE COPY**

85 4 19 023

## UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER 1	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Electrochemical Studies in Liquid Crystals		5. TYPE OF REPORT & PERIOD COVERED Technical
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s)  Robert D. Mariani, Angela Serra, Hector D. Abruna		8. CONTRACT OR GRANT NUMBER(s)  N00014-84-K-0656
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry Cornell University Ithaca, New York 14853		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS  NR 627-844
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research 800 N, Quincy Street Arlington, VA 22217		12. REPORT DATE April 10, 1985
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		13. NUMBER OF PAGES 4
		15. SECURITY CLASS. (of this report)  Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report)  This document has been approved for public release and sale; its distribution is unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number)  Liquid crystals, electrochemistry, oriented layers		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number)  The electrochemical characterization of room temperature nematic phase liquid crystals has been performed in order to identify suitable candidates that will serve as solvents in electrochemical systems. In acetonitrile solvent, we find that the working potential ranges for 4-methoxybenzylidene-4'-n-butyylaniline (MBBA), 4-methoxy-4'-butylazoxybenzene (MBAB) and 4-pentyl-4'-cyanobiphenyl (K-15) are +1.2 - -1.8 V (vs. SSCE), +1.4 - -1.5 V and +1.6 --1.8 V, respectively. Similar results are obtained for the neat phases used as solvents, however, in order to maintain a liquid crystalline phase, the electrolyte concentration		

*CONT'D*

needs to be kept under 40 millimolar.

The electrochemical response of tetracyanoethylene (TCNE), tetracyanoquinodimethane (TCNQ), Ru(bpy)<sup>(2+)</sup><sub>3</sub>, ferrocene and other redox systems has been investigated in these phases. In general, we find large ohmic drops due to the very high resistance of these materials and in order to mitigate these effects, we are exploring the use of microelectrodes.

The effect of orientation on the electrochemical behavior of TCNE has been investigated and the preliminary results seem to indicate a difference in the formal potentials for parallel and perpendicular orientation. In order to better quantify these results, we are developing reference electrodes that will be compatible with these materials.

Accession For	
NTIS GRA&I <input checked="" type="checkbox"/>	
DTIC TAB <input type="checkbox"/>	
Unannounced <input type="checkbox"/>	
Classification _____	
By _____	
Distribution/ _____	
Availability Codes _____	
Dist	Avail and/or Special
A-1	



One of the central goals of electrochemical research is to control the reactivity of substrate molecules at the surface of an electrode. In electrochemical systems, reactivity is strongly affected by the nature and properties of the electrode/solution interface, the potential distribution at the interface, specific interactions between the electrode and the substrate, solvent affects and transport rates.

We have focused our attention on ascertaining the effect of using highly structured solvents as media in which to perform electrochemical experiments; specifically, the use of liquid crystals. Within this broad family of materials, room temperature nematic phases appear especially attractive from an experimental point of view.

With this in mind, we have performed the electrochemical characterization of 4-methoxybenzylidene-4'-n-butylaniline (MBBA), 4-methoxy-4'-butylazoxobenzene (MBAB) and 4-pentyl-4'-cyanobiphenyl (K-15) in acetonitrile solvent and as neat phases in order to ascertain the potential window accessible for electrochemical experimentation. In acetonitrile solvent with tetra n-butyl ammonium perchlorate, we find that these materials have a useful potential window that typically spans over three volts. The specific values are given in Table I.

TABLE I  
Electrochemical characterization of MBBA, MBAB and K-15  
in Acetonitrile

	Oxidationa	Reductiona
1. MBBA	+1.2	-1.8
2. MBAB	+1.4	-1.5
3. K-15	+1.6	-1.8
a. in volts vs. SSCE		

Similar results were obtained when using the neat phases as solvents. In this case, however, a number of difficulties were encountered. First of all a number of electrolytes had to be screened in order to identify those which were sufficiently soluble to be rendered useful in this application. For MBBA and

MBAB we have found that potassium tetrafluoroborate ( $KBF_4$ ) with the potassium ion complexed with Kryptofix 2,2,2 is quite effective whereas for K-15, tetra n-butylammonium tetrafluoroborate (TBAF) proved to be the best. For all systems, the concentration of electrolyte had to be maintained below 40 millimolar in order to retain the liquid crystallinity of the system. Above this concentration, the liquid crystals turned transparent, consistent with the rupture of the liquid crystalline phase.

A representative voltammogram (at 50 mv/sec.) for a platinum electrode in contact with a solution of K-15 with 30.1 mM TBAF is shown in figure 1, and as can be seen, there is a broad potential range where electrochemical experiments can be performed.

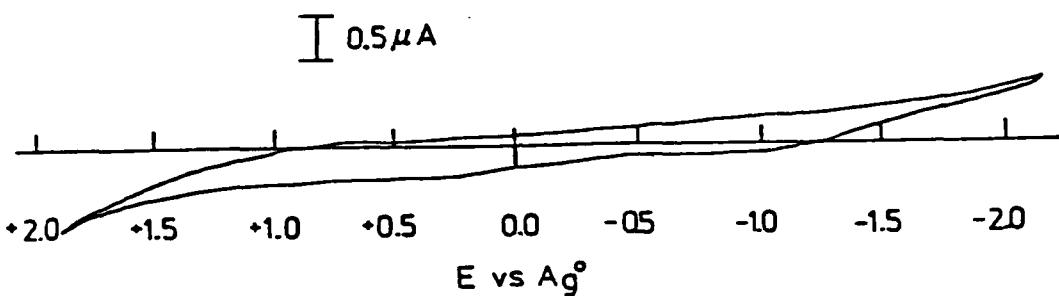


Figure 1

Figures 2 A-C show voltammograms (at 10 mv/sec.) in K-15 30mM TBAF for A.  $[Ru(bpy)_3]^{+2}$ , B. TCNE and C. TCNQ. Although well defined electrochemical waves can be observed, it is clear that there are large ohmic drops. In order to ameliorate this situation, we have begun using small area electrodes (25 micron diameter platinum electrodes) which will exhibit much smaller iR drops.

We have also performed some preliminary studies on the effect of orientation on the electrochemical response of TCNE. In general we find that the formal potential for reduction will vary depending on whether the liquid crystal is oriented

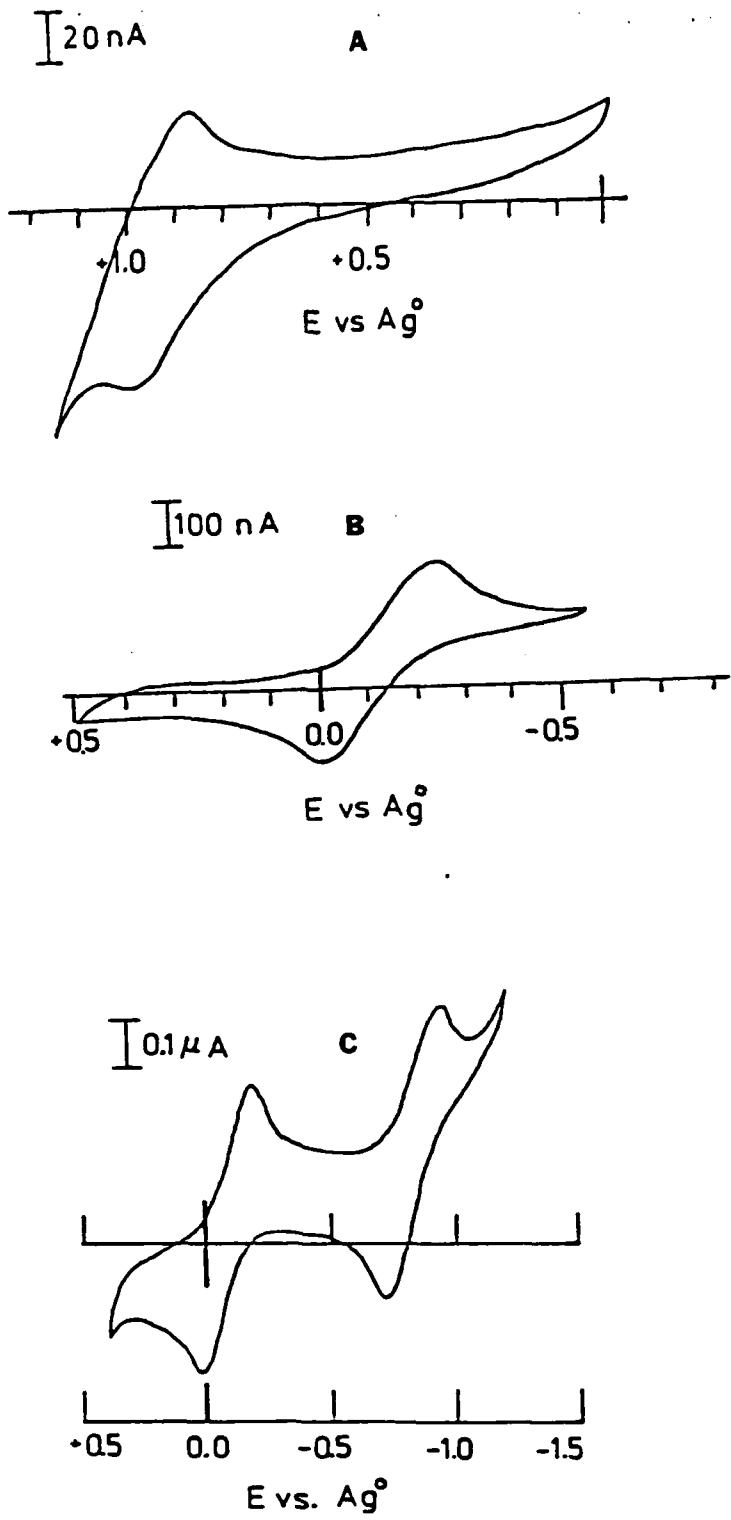


Figure 2

parallel or perpendicular to the electrode surface. There is some variation on the magnitude of this effect and we believe this to be due, at least in part, to the interaction of the TCNE with the silver quasi-reference electrode. As such we are currently exploring the use of alternate materials as reference electrodes.

As an alternate way of maintaining a proper potential calibration, we have performed experiments with TCNE in K-15 where ferrocene has been added. Since the ferrocene potential is not expected to exhibit any significant orientational effect (and in fact, we determined this to be the case) its potential can be used as an internal standard. An example of such an experiment is shown in figure 3. In general we find that with this approach, much more reproducible results can be obtained.

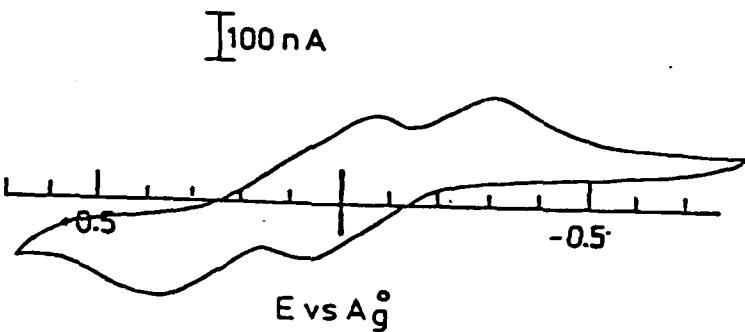


Figure 3

We are currently pursuing the use of microelectrodes (to minimize iR drops) and new reference electrode materials in an effort to better quantify the magnitude of the observed effects. We are also performing the electrochemical characterization of other redox couples that we would expect to have a strong interaction with these liquid crystalline phases.

---

This work was supported in part by the Office of Naval Research

**END**

**FILMED**

**6-85**

**DTIC**